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TITLE: Method for bonding two surfaces together

Abstract Text (1):

Certain organic polymeric materials are capable of reversibly accepting or donating electrons from a reducing entity. The redox sites in the polymer accept electrons and, as a result, a change in the properties of the polymer occurs. This change is useful in modifying or etching the polymeric material. The material can be modified by incorporation of metallic seeds into the material at a controlled depth. The seeds are incorporated by interaction of cations of the metals with the redox sites in the polymer, which cause the reduction of the cations to form the neutral metallic seeds. Subsequent exposure of the polymeric material containing the seeds to an electroless bath causes further deposition of metal having the desirable characteristic of good adhesion to the polymeric material. Etching of the polymeric material can be carried out as a result of an increase in solubility of the polymer in aprotic solvents when its redox sites have accepted electrons. The increased solubility allows openings to be etched in certain areas of the polymeric material that have been reduced, leaving other areas unchanged.

Brief Summary Text (3):

In particular, the present invention is concerned with conditioning organic polymeric materials that are capable of transporting electrons and ions in a reversible manner such as polyimides and polyesters. The method of the present invention is especially advantageous for the processing of electronic devices.

Brief Summary Text (5):

In the manufacture of printed circuit cards and boards, a dielectric sheet material is employed as the substrate. A conductive circuit pattern is provided on one or both of the major surfaces of the substrate. In order to plate on the substrate, it must be seeded or catalyzed prior to the deposition of metal thereon. Included among the various dielectric materials suggested for such purpose are various organic polymers including polyimides.

Brief Summary Text (9):

However, the methods of catalyzing, or seeding, various organic polymer substrates and particularly polyimide substrates, have not been entirely satisfactory and improvement in the degree of adhesion of the final metal layer to the substrate has been less than desired.

Brief Summary Text (10):

In the packaging of semiconductor chips, polyimide films are often coated onto substrates. For instance, in the formation of multilayer substrates for mounting chips, one configuration employs an insulating substrate of a ceramic material onto which is deposited a pattern of metallic conductors. Usually, the conductors are three layers of metal being a layer of chromium, followed by a layer of copper, followed by an overlying layer of chromium. On top of the metallized ceramic substrate is placed a layer or film of a polyimide, and on top of the polyimide a second layer of a pattern of conductors is provided.

Brief Summary Text (11):

The metal contacting the polyimide on the second or subsequent layers can be, for

. instance, copper as disclosed in U.S. Pat. No. 4,386,116 to Nair, et al. and assigned to International Business Machines Corporation, the assignee of the present application, disclosure of which is incorporated herein by reference.

Brief Summary Text (12):

However, the adhesion between the copper and polyimide is not entirely satisfactory and could stand a degree of improvement. In particular, problems have occurred at the copper-polyimide interface resulting in lifting up of the copper line from the underlying polyimide substrate rendering the carrier unsuitable for its intended purpose.

Brief Summary Text (13):

Accordingly, in order that the configurations which involve a copper-polyimide interface be competitive in a commercial environment, it is necessary to improve the adhesion at the copper-polyimide interface.

Brief Summary Text (14):

Another use would be as a dielectric and/or circuit carrier for flexible circuits. This could involve spray coating or roller coating polyamic acid onto a sheet of metal (such as stainless steel or aluminum). The film is then cured or imidized, resulting in a film which is fully or substantially fully cured. The metal which the polyimide is on can be imaged, removed, or maintained. On top of the polyimide, three layers of metal are deposited such as by either evaporation or sputtering. The conductors are chromium or nickel, followed by a layer of copper, followed by a layer of chromium or nickel. By means of photolithographic operations, this metal is imaged into circuits. Depending on the use of the circuit, the cured polyimide may or may not be imaged, either before or after the formation of the circuit.

Brief Summary Text (15):

Flexible circuits may also be fabricated using free-standing polyimide films onto which metal layers are vacuum deposited, laminated, or glued. The metal circuit pattern is defined by using a photoresist pattern to either act as a plating mask or act as a mask for subtractive etching of the metal layer. Through-holes in the polyimide film can be made by drilling, punching, or etching.

Brief Summary Text (16):

In addition, the selective etching of fully imidized polyimide films to provide openings or vias therein is important for various uses of polyimide. For instance, in the packaging of semiconductor chips, polyamic acid films are often coated onto substrates and then cured either chemically or thermally.

Brief Summary Text (17):

In a number of these situations, it is necessary to form vias in the polyimide layer to allow for electrical connections to be made between the different layers of metallurgy. In order that the interconnection be as accurate as possible, it is necessary that the polyimide films be fully cured to avoid distortion of the desired polyimide pattern and prevent attack from other wet processing chemicals.

Brief Summary Text (18):

For instance, in the formation of multi-layer substrates for mounting chips it is necessary to electrically contact some of the conductors in the upper or second layer of metallization to some of the conductors on the lower or first layer of metallization. In order to do so, the polyimide must be selectively etched to form the desired vias therein to allow for metal connection between the upper and lower levels of metallization and connection to a chip and/or board.

Brief Summary Text (19):

Wet etching fully of substantially fully cured polyimide may be accomplished using either hydrazine hydrate, ethylenediamine, or concentrated caustic solutions. These are dangerous chemicals and are avoided by industry wherever possible. Ethylenediamine is highly toxic and irritating and hydrazine hydrate causes blindness and is extremely explosive. Concentrated solutions of sodium or potassium hydroxide are highly corrosive and can cause severe burns. If used, all three methods would require tools which are extremely expensive because of safety concerns.

Brief Summary Text (20):

It would, therefore, be desirable to provide a process for etching of fully cured or substantially fully cured polyimide that is relatively fast without requiring dangerous or explosive chemicals.

Brief Summary Text (22):

The present invention provides a method for treating certain organic polymeric materials in order to provide a metallic layer deposited thereon from an electroless plating bath. Moreover, the present invention provides for enhanced adhesion of the metal to the polymeric material. A further aspect of the present invention is concerned with rendering these organic polymeric materials readily etchable in aprotic solvents to thereby provide etching processes that are relatively easy to control and do not require hazardous chemicals.

Brief Summary Text (28):

A further aspect of the present invention is concerned with etching an organic material wherein the organic polymeric material is capable of transporting electrons electrons to the redox sites of the polymeric material and then dissolving the polymeric material in its reduced form into an aprotic organic solvent. The electrons are supplied to the redox sites of the polymeric material by means of a cathode in an electrochemical circuit, the potential applied to the cathode being equal to or negative of the reduction potential of the polymer or preferably by means of a reducing agent in solution, the oxidation of the reducing agent being negative with respect to the reduction potential of the polymer. The polymeric material is then dissolved in an aprotic organic solvent. Alternatively, the electrons can be supplied to the redox sites of the polymeric material by contacting the polymeric material with tetrakis(dimethylamino)ethylene.

Brief Summary Text (32):

The organic polymeric materials treated pursuant to the present invention must be capable of transporting electrons in a reversible manner. In particular, such polymers include polyimides, polyviologens such as polyxylylviologen, polyphthalocyanine, vinylpyridine-containing polymers, polyamides, polysulfones, certain polyquinolines described in PCT International Publication No. WO83/02368, polyacetylenes, polyesters, such as polyterephthalates, and preferably the polyimides. The polyimides are preferred in view of their continually expanding use in providing electronic devices and packaging and in view of their widespread availability. Discussion of various electrochemical properties concerning polyimides can be found in U.S. Pat. No. 4,512,855 to Mazur; Haushalter, et al., "Thin Solid Films", 102, 161 (1983); Mazur, et al., "Electrochemistry of Aromatic Polyimides", Journal Electrochemical Society, Electrochemical Science and Technology, pp. 346-353, February 1987; and Mazur, et al., "Electrochemical Growth of Metal Interlayers and Polyimide Film", Journal of Physical Chemistry, 1986, 90, pp. 1365-1372.

Brief Summary Text (36):

The polyimides that can be treated in accordance with the present invention include unmodified polyimides, as well as modified polyimides such as polyester imides, polyamide-imide-esters, polyamide-imides, polysiloxane-imides, as well as other mixed polyimides. Such are well-known in the prior art and need not be described in any great detail.

Brief Summary Text (37):

Generally, the polyimides include the following recurring unit: ##STR1## where n is an integer representing the number of repeating units to provide a molecular weight usually about 10,000 to about 100,000. R is at least one tetravalent organic radical selected from the group consisting of: ##STR2## R.sub.2 being selected from the group consisting of divalent aliphatic hydrocarbon radicals having from 1 to 4 carbon atoms and carbonyl, oxy, sulfo, sulfide, ether, siloxane, phosphine oxide, hexafluoroisopropylidene and sulfonyl radicals and in which R.sub.1 is at least one divalent radical selected from the group consisting of an aliphatic organic radical or from the group shown: ##STR3## in which R.sub.3 is a divalent organic radical selected from the group consisting of R.sub.2, silico, and amino radicals. Polymers containing two or more of the R and/or R.sub.1 radicals, especially multiple series

of R.₁ containing amido radicals, can be used.

Brief Summary Text (38):

Polyimides are available commercially from a variety of suppliers in one of three forms: a) as solutions of the polyamic acid precursors (e.g., DuPont Pyralin.RTM.); b) as pre-imidized polyimide film (e.g., DuPont Kapton.RTM. film); or c) as pre-imidized powders (e.g., Ciba-Geigy Matrimid 5218.RTM.) or solutions (e.g., Ciba-Geigy Probimide). The chemistry of commercial Polyimides includes examples of many of the components listed above, but a preferred polymer for use pursuant to the present invention is based on the monomers pyromellitic dianhydride (PMDA) and oxydianiline (ODA, also named 4,4'-diaminodiphenyl ether). Other preferred polymers for use pursuant to the present invention are the polymers of benzophenonetetracarboxylic dianhydride (BTDA) and ODA and/or 1,3-phenylenediamine and the polymer of 3,3'-biphenylenetetracarboxylic acid (BPDA) and 1,4-phenylenediamine (PDA). Polyimide films based on PMDA-ODA are available from Allied Corporation under the tradename Apical.RTM. and from Du Pont under the tradename Kapton.RTM.. Films based on BPDA-PDA are available from Ube Corporation as Upilex.RTM. and from Hitachi Chemical Company as PIQ-L100. Other tradename Polyimides useful pursuant to the present invention include Durimid.RTM. from Rogers Corporation and the Du Pont Pyralin.RTM. series, including PI-2525 and PI-2566. The Upilex.RTM. Polyimides, although possessing higher thermal and dimensional stability than that of the Kapton.RTM. Polyimides, have not been widely used in integrated circuit packaging because of the absence of efficient wet etching processes for such Polyimides.

Brief Summary Text (40):

The present invention is capable of etching these Polyimides as well as other difficult to etch, fully imidized Polyimides.

Brief Summary Text (42):

In order to facilitate understanding of the present invention, the details of the processes will be discussed with specific reference to Polyimides. With respect to the Polyimides, the bis-imide functional groups of the polymer can be reduced (by one electron) to the radical anion, or reduced (by two electrons) to the dianion or diradical dianion, or reduced (by three electrons) to the radical trianion as illustrated in the following reaction scheme for 3,3',4,4'-benzophenone tetracarboxylic diimide functional group where e.sup.- is an electron and C.sup.+ is a counter cation. ##STR4##

Brief Summary Text (43):

According to preferred aspects of the present invention, the reduction is achieved by means of a reducing agent that has an oxidation potential negative with respect to the reduction potential of the polymer. With respect to Polyimides, compounds such as benzil anion, anthraquinone anion, benzophenone anion, benzoin dianion, sodium naphthalenide, anion of N,N'-di-n-butylpyromellitimide and even solvated electrons generated, for example, in liquid ammonia can be used as the reducing agent.

Brief Summary Text (47):

The compounds can be reduced electrochemically or by bulk electrolysis. Typically, this is done using a two-compartment cell. Whereby the compartments are separated by a sintered glass disk or frit having a porosity of less than 8 .mu.m. A salt bridge or semi-permeable membrane also could be used to separate the compartments. The working compartment is housed with a cathode electrode which is comprised of a metal such as platinum, mercury, or stainless steel. The anode electrode is comprised of a conductor such as platinum, carbon, or stainless steel. For potentiostatic operation, an appropriate reference electrode is positioned in the working compartment (e.g., Ag/0.1M Ag NO₃). The cell can be purged with an inert gas such as N₂ or argon using an inlet tube and one-way valve or operation can be done in a glove box under an inert atmosphere.

Brief Summary Text (55):

The Polyimide, which, after being reduced by the reducing agent contains a region of reduced Polyimide near the exposed surface, can then be exposed to a solution of the metal ion in order to provide the metallic sites or seeds for subsequent metallic

plating.

Brief Summary Text (56):

In particular, the solution can contain a cation of the desired metal such as palladium, platinum, silver, gold, copper, cobalt, and nickel which will contact the redox sites of the polyimide. The redox sites, which are in the reduced state, will thereby transfer electrons to the cation to reduce it to metal atoms in the zero oxidation state.

Brief Summary Text (62):

In addition, an alternative process can be used for depositing the seed metal. In this case, the polymer film is contacted with a solution of the metal cations in a solvent which will cause swelling of the polymer film and concurrent absorption of metal cations. Exposure of the swollen film to a solution of the reducing agent can then cause reduction of the seed metal cations to the metallic state. It is preferable to wash any salt from the surface of the polyimide film prior to contact with the solution of the reducing agent. The depth or positioning of the metal deposition will then depend on the relative rate of diffusion of the electrons from the reducing agent into the film versus that of the cations out of the film. These rates are controllable by adjusting the concentrations of the reactant and, therefore, the position of the metal ions beneath the surface for good adhesion can be readily controlled.

Brief Summary Text (69):

The first electron reduction potential E.degree. for various polyimides are given:

Brief Summary Text (73):

In fact, one use of the process of the present invention involves repairing pinhole defects in sputtered or evaporated metallic layers on an organic film. An example of such problem is that during production of certain polyimides in a roll format, slip agents (inorganic grains) are put onto the polyimide surface to make processing and handling of the material easier by reducing the amount of "sticking". These slip agents can be found up to 1 mil in diameter and can cause problems in the subsequent processing of the material, such as discontinuities in sputtered metal deposits. Other contaminants such as dust, lint, oils, and greases can introduce voids in the sputtered metal layer.

Brief Summary Text (74):

In order to obtain acceptable adhesion of copper circuitry to polyimide, expensive and complicated evaporation schemes are used. A layer of chromium metal is used as an adhesion layer, followed by evaporation of copper to provide a plating base layer for depositing thicker metal. The presence of this slip agent causes voids in the sputtered or evaporated metal layer and hence, a non-continuous plating base. Since the plating base also serves as a polyimide etch mask in certain applications, voids in the metal layer expose the polyimide in areas where etching is not wanted. A method is described by which voids in sputtered or evaporated metal layers can be metallized to form a continuous metal film.

Brief Summary Text (78):

Also, if desired, the vias or through-holes can be selectively metallized. For example, to selectively metallize only a via or through-hole, a dielectric substrate is coated with a material or resist which can not be activated by the process described above. Through-holes or vias can be made by patterning the resist and etching the structure or laser ablation through the resist material and dielectric. Hence, only the region in the through-hole is reduced, seeded, and plated in this process. Selective metallization of the via or through-hole wall is obtained by having an appropriate photoresist or other material on the polymer surface which does not seed or can be removed (lift-off) following the seeding process. Another approach involves coating a patterned resist with another resist which protects the under-resist from the seeding process.

Brief Summary Text (79):

Silicon nitride can be used as a mask for selective seeding. It has also been observed that when polyimide is exposed to reactive ion etching (RIE), it does not undergo effective seeding according to the present invention, probably due to

oxidation of the polyimide surface. Furthermore, polyimide exposed to RIE can again be rendered susceptible to seeding according to the present invention by, for example, treatment in a gas environment of about 3-10% hydrogen in nitrogen for about 15-30 minutes. Therefore, the polyimide exposed to RIE can be used as a mask for selective seeding of such polyimide which has subsequently been treated in a gas environment described above, or by polyimide not previously exposed to RIE.

Brief Summary Text (88):

The plating baths generally have a specific gravity within the range of 1.060 to 1.080. The temperature of the bath is usually maintained between 70.degree. C. and 80.degree. C. and more usually between 70.degree. C. and 75.degree. C. The O.sub.2 content of the bath is generally contained between about 2 ppm and about 4 ppm and more usually about 2.5 ppm to about 3.5 ppm by injecting oxygen and an inert gas into the bath. The overall flow rate into the bath is usually from about 1 to about 20 SCFM per thousand gallons of bath. In addition, the polymers in the reduced state obtained in the manner disclosed above and especially the polyimides can be readily and selectively etched by dissolving the reduced polymeric material in an aprotic organic solvent.

Brief Summary Text (89):

The dissolution or etching of partially to fully imidized or cured polyimides is based on reduction of the polyimide by either direct electrochemical reduction at an electrode surface or through chemical reduction using a reducing agent in an electrolyte solution in contact with the polyimide film. Also, the polymeric material can be treated by providing electrons by contacting the polymeric material with TKDE. Unlike the wet etching methods involving hydroxide or hydrazine, the present approach exploits the ability of polyimide to undergo reversible electron transfer.

Brief Summary Text (90):

Polyimide films which are cast, laminated, or deposited onto a conductive substrate would act as a polyimide modified electrode and could be electrochemically reduced in an electrolyte solution.

Brief Summary Text (91):

The preferred method for etching polyimide films (those free-standing or present on a substrate) is by chemical reduction. This process utilizes the reversible redox behavior of polyimides to generate the reduced bisimide forms as described for polyimide film reduction above. For chemical reduction there is no electrode or external circuit to "directly" supply the electrons. Instead, dissolved reducing species or agents in the electrolyte are the source of electrons. A fundamental requirement for the reductant is that it have a sufficiently negative reducing power or potential to allow electron transfer to thermodynamically take place. It is also important that the kinetics of the electron exchange are not inhibiting. The chemical etching method has the advantage over electrochemical etching because complete film electroactivity is not required since any bisimide groups coming in contact with the reducing solution will undergo electron transfer causing solubilization of the polymer.

Brief Summary Text (93):

The polyimides dissolve into the solvent in the reduced form. UV-Vis analysis of the resulting solution show that the dissolved species are present in the reduced states. The most effective solvents for dissolving the reduced polyimides are aprotic polar solvents, including amides (N-methyl-2-pyrrolidone, N,N-dimethylformamide and dimethylacetamide), oxides (N,N-dimethylsulfoxide), cyclic esters (propylene carbonate, .gamma.-butyrolactone), and nitriles (acetonitrile). The etch solution will also contain a supporting electrolyte salt of the type discussed above. Profiling or two-dimensional patterning of the polyimide can be accomplished by using a photoresist such as Waycoat SC or KTFR (or other ion barrier mask) pattern on the polyimide prior to polyimide reduction.

Brief Summary Text (94):

The etching process of the present invention is especially advantageous since it can be used to etch difficult to etch polyimides such as the fully cured or imidized polyimides, for example, the Upilex.RTM. polyimides.

Brief Summary Text (95):

Patterned etching, according to the present invention, results in anisotropic etching with the sidewalls of the etched area being tapered inwardly as the etching proceeds through the depth of the material.

Brief Summary Text (96):

In addition, it has been found, according to the present invention, that the use of photoresists as the mask for selective etching results in some undercutting of the mask by the etchant. However, it has been found, according to certain preferred aspects of the present invention, that this undercutting can be at least significantly reduced, if not entirely eliminated, by employing a conductive metal as the etch mask. The use of a metal mask results in anisotropic etch with the sidewalls being tapered inwardly as the etching proceeds downward in the substrate.

Brief Summary Text (97):

In view of the anisotropic profile achieved by the selective etching according to the present invention, through-holes having a V-shaped configuration with the apex of the V being open. In fact, a sandwich of two or more substrates can be etched from both sides, resulting in a V-like profile from each surface converging towards each other with the apex of each V being open to some extent. The V-like tapered through-holes are desirable since such can lead to enhanced plating.

Brief Summary Text (98):

Moreover, with respect to etching, there is no swelling of the remaining polymer as experienced with other wet etching techniques.

Brief Summary Text (99):

A further aspect of the etching is that different polymers such as even different polyimides can have different reduction potentials. Because of this, reducing agents can be utilized with a reduction potential sufficiently negative to allow electron transfer to take place with one type of polymer, but not sufficiently negative to reduce another polymer. In fact, even the same polymer at different cure levels can have different dissolution rates. In other words, the same polymer at a different cure level can be used as the etch stop.

Brief Summary Text (100):

A further aspect of the present invention is bonding polymeric materials together. For instance, an important concern for many uses is adhesion between polyimide layers. This is an especially difficult problem since polyimide-to-polyimide adhesion is poor due to the chemical inertness and unreactivity of these materials. The interface must also be absent of voids since contaminants can be introduced along crevices which leads to premature device failure.

Brief Summary Text (101):

The present invention bonds two polymeric materials together without creating a distinct interface between the materials. In particular, the process comprises supplying electrons to redox sites of the polymeric material of both surfaces to create reduced regions therein. The organic polymeric materials are capable of transporting electrons in a reversible manner. As an example, adjacent polyimide surfaces are reduced to generate anionic forms of the polymer.

Brief Summary Text (102):

The anionic forms of polyimides are soluble and dissolve in the reduced state while remaining a polyimide. In the reduced form, two surfaces can dissolve into each other, allowing the polymeric chains to interpenetrate.

Brief Summary Text (103):

The treated surfaces are then brought together with the reduced regions of each adjacent to each other such as by laminating or pressing the surfaces containing the reduced regions together. The reduced regions are permitted to interpenetrate and form an interphase. It has been observed that the reduced polyimide dissolves or dissociates from the polymer matrix in the solvent present in the reducing step. In the case of a polyimide, following reduction, the polyimide is dissolved in the imidized form (i.e. - the polyimide is essentially intact and present as a polyimide

.and not a polyamic acid salt or ring opened structure). This condition allows the two reduced surfaces to interpenetrate. Once the polyimide surfaces have merged into an interphase region, oxidation of the reduced polymer renders the polyimide insoluble and fuses the polyimides together. The residual solvent can be evaporated at elevated temperature and reduced pressures. The entrapped counter-ions are inert and immobile in the polyimide matrix under humid environments which the structure is likely to encounter in service. The advantage of the disclosed approach over chemical conversion or reaction of the polyimide structure is that no polyimide chemistry is required following joining since direct electron transfer regenerates the original polyimide state.

Brief Summary Text (104):

The adhesion of polyimide-to-polyimide is especially significant in thin film structures fabricated by parallel process techniques. In the parallel process scheme, thin film structures comprised of circuitized polyimide layers are stacked (or interconnected) to provide a multilevel wiring structure. The multilevel structure results in a large area where polyimide of one level contacts polyimide of another. Therefore, it may be critical that the polyimide/polyimide interface be structurally sound.

Brief Summary Text (105):

Adhesion between polyimide layers can be accomplished through the use of adhesives such as epoxy or acrylic based glues. However, the use of an adhesive introduces an additional material and layer. Furthermore, most adhesive expel solvents and other materials during curing. An alternative approach is to modify the polyimide polymeric structure at the surface to provide highly reactive or energetic bonding sites. Chemical conversion of the polyimide, however, might result in changes in the physical/dielectric properties of the polyimide. This joining results in an interphase region of polyimide providing a continuous transition between the bulk of the two adjacent polyimide layers. This process does not introduce an interface, nor require an adhesive material, or alter the polyimide chemistry.

Detailed Description Text (4):

5 mil thick Kapton (PMDA-ODA) polyimide films measuring 2 inches.times.4 inches are exposed to the benzil reducing agent solution for 15 seconds, 30 seconds, 2 minutes, and 4 minutes to reduce the Kapton.RTM. surface to the radical anion form. The films are rinsed with acetonitrile to remove any residual material from the surface of the substrate. Next, the films are immersed in a N,N'-dimethylformamide (DMF) solution containing about 0.05M PdCl₂ for 1 minute, resulting in Pd metal deposition and oxidation of the reduced polyimide surface to the neutral form. The surface is not electrically conductive after Pd deposition.

Detailed Description Text (9):

These copper coated Kapton.RTM. films are then heated at 90.degree. C. under vacuum for 1 hour. Laminar UF (Dynachem) dry film photoresist (1.5 mil thick) is laminated to both sides. A line peel pattern is exposed through a mask and the photoresist developed in a sodium bicarbonate solution. The photoresist patterned substrates are electrolytically copper plated using a solution composed of 60 gm/L CuSO₄.5H₂O and 30 ml/L concentrated H₂SO₄ in water at a rate of 15 mA/cm² to increase the copper thickness to about 17 .mu.m. The photoresist is stripped using 8% KOH in water solution and the electroless copper strike layer between the peel lines removed using dilute FeCl₃ in H₂O solution. Peel tests (90.degree.) using 30 mil wide copper lines show-that the adhesion between the copper and the Kapton.RTM. substrate is about 37 to 52 g/mm, the average being 42 g/mm with cohesive failure occurring within the polyimide.

Detailed Description Text (12):

Polyimide (PMDA-ODA) films are prepared by spin coating polyamic acid, 10.7% in N,N-dimethylacetamide solution at 1200 and 2000 rpm onto stainless steel and silicon substrates. The films are then heated to 85.degree. C. for 10 minutes.

Detailed Description Text (13):

The polyimide is thermally cured by heating at 150.degree. C., 250.degree. C., and 400.degree. C. maintained for 60 minutes at each temperature to yield fully imidized films and which are 8.1 .mu.m (2000 rpm) and 12.9 .mu.m (1200 rpm) thick.

Detailed Description Text (16):

Thermid 630.RTM. polyimide films derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride, available from National Starch and Chemical Company, are prepared by spin coating a 5% solution in N,N-dimethylacetamide onto silicon substrates. The films are cured by heating at 200.degree. C. for 1 hour which give a final thickness of 3.9 .mu.m.

Detailed Description Text (17):

Thermid.RTM. polyimide films are exposed to a benzil reducing solution as in Example 1 for 60 seconds and then rinsed with acetonitrile. Next, they are immersed in a solution containing 0.001M PdCl₂ in ACN for 60 seconds. Exposing the Pd seeded films to an electroless copper plating solution as described in Example 1 for 2 minutes yields shiny copper deposits on the Thermid.RTM. polyimide surface.

Detailed Description Text (19):

A solution composed of 0.05M anthracene and 0.1M TBAFB in DMF is reduced at a rate of 50 mA under galvanostatic conditions until about 10% of the anthracene is reduced. 2 mil thick Upilex.RTM. polyimide films measuring 3 inches.times.4 inches are immersed in the anthracene reducing solution for 2 minutes which caused the films to become dark blue-green due to surface reduction. The reduced films are rinsed using ACN and then exposed to a solution containing 0.002M PdCl₂ in acetonitrile for 60 seconds. The Pd seeded films were rinsed with acetonitrile, dried, and then held for 80 seconds in an electroless copper plating solution of the type disclosed in Example 1. This treatment results in a uniform, highly reflective copper deposit on the surfaces.

Detailed Description Text (22):

Kapton.RTM. polyimide (2 mil) immersed for 30 seconds in the solution prepared above, then rinsed with acetonitrile is exposed to a 0.001M PdCl₂ /ACN solution. The Pd seeded Kapton.RTM. is active towards electroless copper plating from a bath disclosed in Example 1.

Detailed Description Text (25):

Kapton.RTM. polyimide (2 mil) immersed for 30 seconds in the solution prepared above, then rinsed with acetonitrile is exposed to a 0.001M PdCl₂ /ACN solution. The Pd seeded Kapton.RTM. is active towards electroless Cu plating from a bath of the type described in Example 1.

Detailed Description Text (27):

Palladium seeded polyimide films as prepared in Examples 1, 2, 6, and 7 using Kapton.RTM., Example 3 using thermally imidized PMDA-ODA, Example 4 using Thermid 630.RTM., and Example 5 using Upilex.RTM..

Detailed Description Text (28):

An electroless nickel plating solution is made using 30 g/L NiCl₂ . 6H₂O; 22 g/L Na citrate, 50 g/L NH₄Cl; 10 g/L Na hypophosphite and adjusted to pH 8.5 using concentrated NH₄OH and held at 85.degree. C. The Pd catalyzed polyimide films as described above are exposed to the electroless Ni plating solution for 2 minutes which results in highly reflective, electrically conductive nickel deposits.

Detailed Description Text (34):

PMDA-ODA polyimide films are prepared by spin coating polyamic acid, 10.7% in N,N-dimethylacetamide at 1200 rpm and 2000 rpm onto stainless steel and conductive SnO₂ glass.

Detailed Description Text (35):

The polyimide is imidized by exposing the coated substrate to an atmosphere saturated with NMP at about 51.degree. C. for 1.5 hours, followed by immersion in an equal volume mixture of anhydrous pyridine and acetic anhydride at 25.degree. C. for 2 hours. The films are then rinsed with methanol and dried at 90.degree. C. under vacuum for 1 hour. The final thickness of the polyimide films are 8.6 .mu.m (2000 rpm) and 13.5 .mu.m (1200 rpm). These coated structures are made into polyimide-modified electrodes by making electrical contact to the conductive layer

on which the polyimide is deposited. Epoxy is used to cover this structure leaving only a region of the polyimide surface exposed.

Detailed Description Text (36):

A PMDA-ODA modified (working) electrode is immersed in a solution composed of 0.1M TBAFB in DMF and held at open circuit for 15 minutes. Next, a potential of -1.0 V vs saturated calomel electrode (SCE) is applied to the working electrode for 10 minutes and then PdCl₂ in TBAFB DMF is added to yield a 0.8 mM PdCl₂ working solution and the electrode potential maintained at -1.0 V for 20 minutes. The electrode is then removed from the cell and oxidized in air. After immersing the sample in an electroless copper plating solution as described in Example 1 for 2 minutes, a bright copper deposit is generated on the polyimide surface.

Detailed Description Text (42):

A solution comprised of 0.0125M benzophenone and 0.1M TBAFB in DMF is reduced until about 10% of the benzophenone is converted to the anion form in a manner similar to that described in Example 16. Kapton.RTM. polyimide etches at a rate of 0.2 .mu.m/min when exposed to this solution.

Detailed Description Text (44):

A solution comprised of 0.05M benzil and 0.1M TBAFB in ACN is reduced at a constant current of 50 mA using a Pt mesh electrode in an electrochemical cell until about 10% of the benzil was converted to the radical anion form. A 2 mil thick Kapton.RTM. film is immersed in the reducing bath for 15 minutes to reduce the polyimide to the radical anion form. The reduced film is then immersed in solution comprised of 0.1M TBAFB in DMF, thus causing dissolution of green colored radical anion form of the polyimide. UV-Vis analysis confirms that the polyimide dissolves in the DMF solution.

Detailed Description Text (48):

A PMDA-ODA polyimide film is prepared on a stainless steel electrode as in Example 14. The polyimide modified electrode is used as the cathode in an electrochemical cell containing 0.1M TBAFB in DMF solution. The cathode is held at a constant potential of -1.8 V vs SCE. The polyimide film initially turns green and then becomes deep purple in color. After 10 minutes in this potentiostatic mode, a soluble purple colored product streams from the electrode surface and after 30 minutes, the film is entirely dissolved. Cyclic voltammetry of the dissolved polyimide solution using a Pt working electrode shows two reversible redox reactions corresponding to reduction of the pyromellitic dianhydride (PMDA) moiety to the radical anion and dianion states.

Current US Cross Reference Classification (2):

156/305

CLAIMS:

1. A method for bonding two surfaces together of organic polymeric material that is capable of transporting electrons in a reversible manner which comprises supplying electrons to redox sites of the polymeric material of both surfaces to cause a reversible electron transfer resulting in the redox state of said sites being in a reduced state; bringing together said surfaces whereby the reduced regions interpenetrate and form an interphase; and then reoxidizing the reduced interphase region to thereby bond the two surfaces together, wherein said organic polymeric material is a polyimide or a polyester.
2. The method of claim 1 wherein said polymeric material is a polyimide whereby said polyimide is cured by any method by which imide ring cyclization can be obtained, including thermal and chemical dehydration curing.
3. The method of claim 2 wherein said polyimide material is a free-standing or supported film derived from a dianhydride selected from the group of pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, naphthalenetetracarboxylic dianhydride, perylenetetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)bis-phthalic anhydride, and

bis(3,4-dicarboxyphenyl)sulfide dianhydride.

4. The method of claim 2 wherein the thickness of said polyimide material is about 100 angstroms to 5 mil.

5. The method of claim 1 wherein said polymeric material is a polyimide and said electrons are supplied electrochemically by a cathode in contact with said polyimide in an electrochemical circuit using an aprotic solvent containing a supporting electrolyte salt.

6. The method of claim 5 wherein the electrochemical reduction of said polyimide is done by either control of the current supply or control of the applied potential.

7. The method of claim 5 wherein said polyimide material is derived from a dianhydride selected from the group of pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, naphthalenetetracarboxylic dianhydride, perylenetetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)-bis-phthalic anhydride, and bis(3,4-dicarboxyphenyl)sulfide dianhydride.